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RESEARCH

Analysis of Anti-Wear Properties of CuO Nanoparticles as Friction Modifiers in Mineral Oil (460cSt Viscosity) Using Pin-On-Disk Tribometer

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A B S T R A C T

The present work investigated the anti-wear properties of CuO nanoparticles based mineral oil using pin-on-disk apparatus. The pin material selected was EN 24(untreated) as it is used in gear manufacturing. Commonly used graphite macro particles (wt.%) and CuO nanoparticles(wt.%) were used as additives. It had been observed that the additives based mineral oil samples exhibited superior antiwear properties than pure mineral oil. Both CuO nanoparticles (0.2 wt.%) and graphite (0.2 wt.%) based lubricant showed significant decrease in coefficient of friction and specific wear rate. There was a reduction in both coefficient of friction (28.5 % approx.) and specific wear rate (70 % approx.) in case of CuO nanolubricants and graphite based mineral oil as compared with the pure mineral oil.Flash-fire point, viscosity and viscosity index also increased with the increase in additive concentration. The surface characteristics of the pin were studied using Scanning Electron Microscope (SEM) and surface roughness tester. The SEM images showed more rough surfaces in case of pure mineral oil samples as compared with graphite and CuO nanoparticles based samples. The surface roughness values of the pins in case of graphite (0.2 wt.%) and CuO nano particles (0.2 wt.%) based lubricant were much lesser than pure mineral oil. From the results predicted minimum 0.2 wt.% CuO nanoparticles were required to enhance the antiwear property of the lubricant. This work aimed in bringing a comparative experimental analysis using CuO nanoparticles and commonly used graphite macro particles as lubricant additives on various properties such as viscosity, flash point, fire point, surface roughness and anti-wear properties. Thus, the work would be useful in developing new nano lubricants with minimum additive concentration.

1. INTRODUCTION

Lubrication is an important concept in the field of tribology. The demand for lubricating oils has been increasing day by day. Thus, the trend of “minimal additivation” has been in focus for all lubricant companies. Among the different types of lubricants, mineral oils are the most commonly used lubricants in process industries. Mineral oil contains nearly 90-95 % base oil and 10-5 % additives. The nano sized additives had attracted the researchers for their superior mechanical and self-lubricating properties. Nano fluids are a new class of engineering fluids which are manufactured by dispersing very fine metallic or non-metallic particles of nano meter dimensions. These nano fluids find their applications where the fluid has to pass through small gaps. The mechanisms which are responsible for improving the tribological behaviour of nanolubricants are: ball bearing effect [1-3], protective film [4-8], mending effect and polishing effect [9]. A novel method of using nanoparticles for in situ nano polishing of surfaces was described by Mosleh et al. [10], who observed a significant increase in film thickness and lower frictional torque. Significant effects were also observed using various other nano particles such as LaF3 [11], carbon nano onions [12], CuO oxide nano particles [13]. An increase in kinematic viscosity and viscosity index of 32.94 % in case of lubricant on addition of single walled carbon nano tube was reported by Valliki et al. [14]. Battez et al. [15] studied CuO, ZrO, ZnO nanoparticles in poly-alpha-olefin oil and predicted a decrease in antiwear properties. The reduction in coefficient of friction and specific wear rate were also observed using MWCNT [16] and CuO [17] in industrial and coconut oils respectively. Vadiraj et al. [22] studied the effects of boric acid and nano CuO additives in different volume proportions using SAE 15W40 and SAE 90 and predicted the increase in COF in case of cast iron and decrease in COF in case gear steel.

The present work aimed in bringing a comparative experimental analysis using CuO nanoparticles as lubricant additives on various properties such as viscosity, flash point, fire point, anti-wear property and minimal quantity additivation. Thus, the present work will be useful in developing new nano lubricants with minimum concentration of additives.

2. MATERIAL SELECTION

2.1 Base oil

The mineral oil of 460cSt had been chosen as it is being used in gear boxes of many process industries.

2.2 Pin material

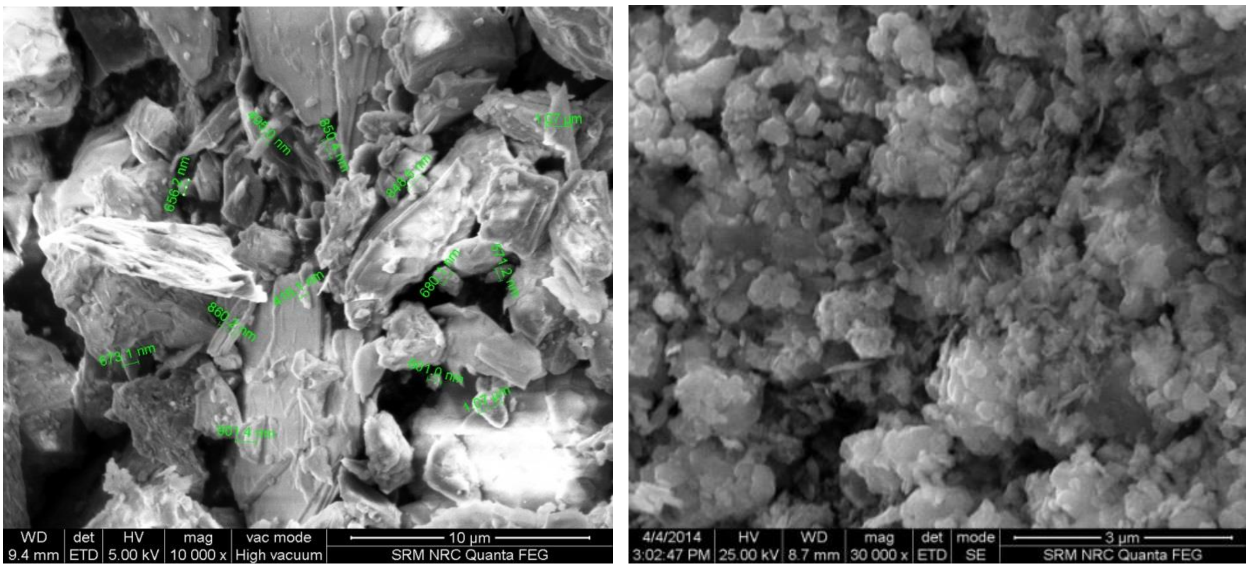
EN 24(untreated) had been chosen as it finds its application in gear manufacturing. The chemical composition of EN 24 is shown in Table 1.

Table 1. Chemical composition (%) of EN 24 pin (ASTM E 415-08).

C	Mn	Si	S	P	Cr	Ni	Mo
0.370	0.533	0.248	0.023	0.027	1.167	1.397	0.214

2.3 Additives

Graphite macro particles and CuO nanoparticles as shown in Fig. 1, were used as additives. Graphite had been chosen as it is the most commonly used additive in almost all industrial lubricants. Graphite particles (0.62-0.86 μm) were procured from the local vendor in Chennai while CuO nano particles (25-55 nm, Stock No.NS6130-03-310) were procured from Nanoshel LLC.



(a) (b)

Fig. 1. SEM images of (a) Graphite macro particles, (b) CuO nano particles.

2.4 Oil Preparation

Graphite macro particles (0.2 wt.%) and CuO nanoparticles (0.05 wt.%, 0.1 wt.%, 0.15 wt.%, and 0.2 wt.%) were selected as friction modifiers. CuO nanoparticles were treated with oleic acid and cyclohexane to have uniform dispersion in the lubricant. Both oleic acid and cyclohexane were each taken to be 10 wt.% of CuO nanoparticles. For each wt.% of additives, 1000 ml mineral oil was used. The nano particles were added to the mineral oil and sonication was done for 45-50 [23] minutes using a bath sonicator and was followed by homogenization for 10 minutes. Since, the main aim of the present work was to compare the tribological properties of the nano additives with macro additives, hence, the optimum concentration for nanoparticles was determined, which was found to be 0.2 wt.% (CuO). Therefore, in order to compare the tribological properties at the maximum wt.% of CuO, 0.2 wt.% graphite macro particles were added. More work would be done in near future by varying the concentrations of graphite particles too.

3. RESULTS AND DISCUSSION

3.1 Viscosity Analysis

Viscosity is one of the important properties of any lubricant. It determines the film formation tendency of the lubricant. Higher the viscosity index (VI), higher would be the film stability at higher temperatures. The viscosity of the samples in the present work had been measured from temperature 40 ^{0}C to 100 ^{0}C using Redwood viscometer. As observed from Table 2, both viscosity and viscosity index increased with the increase in concentration of additives [19-21]. This was due to the fact that with the increase in concentration of nanoparticles the internal shear stress of the lubricant increased due to which the viscosity also increased. It was also observed that with the increase in temperature the viscosity of nanoparticles based lubricant decreased (Table 2). This may be due to the weakening of inter-particle and inter molecular adhesion forces.

As observed from Table 2 and Fig. 2, the viscosity and viscosity index of CuO nanoparticles based lubricant (Table 2) were found to be higher than pure mineral oil and mineral oil + graphite. Thus, the CuO nanoparticles based lubricant would have a better film forming tendency at higher temperatures as compared to graphite and the pure mineral oil.

Table 2. Viscosity and viscosity index.

Sample	40 ^{0}C	60 ^{0}C	80 ^{0}C	100 ^{0}C
MO	460	151.1	62.5	29.0
MO +0.2 wt.% Graphite	553.4	179.9	70.9	34.0
MO +0.05 wt.% CuO	548.3	177.0	69.4	35.0
MO +0.1 wt.% CuO	574.9	182.1	72.3	37.21
MO +0.15 wt.% CuO	601.6	188.8	76.8	39.48
MO +0.2 wt.% CuO	629.08	195.54	82.0	42.2

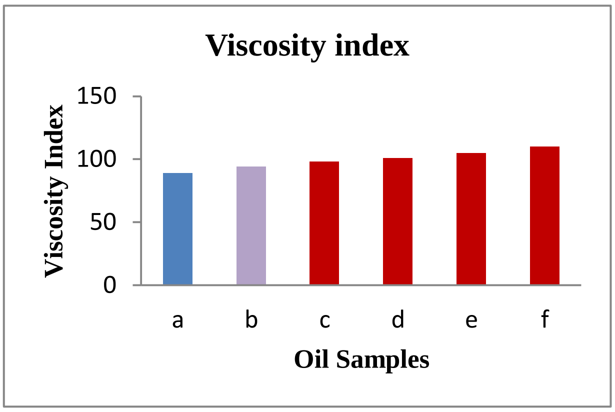


Fig. 2. Coefficient of friction of (a) pure mineral oil, (b) mineral oil+0.2 wt.% graphite, (c) mineral oil+0.05 wt.% CuO nano particles, (d) mineral oil+0.1 wt.% CuO nano particles, (e) mineral oil+0.15 wt.% CuO nano particles, (f) mineral oil+0.2 wt.% CuO nano particles.

3.2 Flash and fire points

As observed from Table 3, the flash point of CuO nanoparticles based lubricants decreased while the fire point increased. An explanation for the decrease in flash point of this phenomenon may be the possible adsorption of both liquids on the surfaces of nanoparticles. When the surfaces of nanoparticles were saturated there was an increase in the concentrations of cyclohexane and oleic acid. This increased the partial tension/pressure of their vapors and reduced the flashpoint temperature (Rault's first law). One more reason may be the adsorption of oleic acid preferentially and thus, with further increase in the concentration of more volatile cyclohexane, there was a drop in the mixture flashpoint.

Table 3. Flash and Fire Point.

Sample	Flash point, ^{0}C	Fire Point, ^{0}C
MO	220	302
MO + 0.2 wt.% Graphite	222	318
MO +0.05 wt.% CuO	218	321
MO +0.1 wt.% CuO	212	320
MO +0.15 wt.% CuO	210	316
MO +0.2 wt.% CuO	208	315

As observed from Table 3, the fire point in case of both graphite and CuO nano particles based lubricants were almost equal but were higher than the pure mineral oil.

3.3. Wear test

The anti-wear tests were carried out using a pin-on-disk tribo-meter (Make: Ducom. Model TR20) in accordance with ASTM G-99 standards). The disc is of EN 31 (hardness 60 HRc). Approximately 5±0.2 mL lubricant was used during the test under 140 N normal load and 0.7 m/sec sliding speed. The pins were 10mm in diameter and 25 mm in length. All pins were cleaned with acetone and dried before and after the tests. In order to maintain thin film/boundary lubrication, oil was supplied drop by drop at the interface in regular intervals of about 2 sec. Each test was performed thrice and the average values of the tests were shown in this work. The sliding wear losses were measured using high precision digital weighing machine. The weight losses of the test samples were converted to volume losses. The specific wear rates were calculated using Archard equation as:

$$W_s = \frac{\Delta V}{Lxd} \qquad (1)$$

where, W_s is specific wear rate (m2/N), ΔV is volume loss (m3), L is load (N) and d is sliding distance (m).

As observed from Fig. 3 and Fig. 4, specific wear rate and coefficient of friction decreased as additives were added to mineral oil. The specific wear rate and coefficient of friction in case of graphite based sample were lesser than pure mineral oil and mineral oil with CuO nanoparticles (0.05 wt.%, 0.1 wt.% and 0.15 wt.%) but were comparable with 0.2 wt.% CuO nanoparticles based lubricant.

Table 4. Anti-wear test (ASTM G99).

Oil Sample	Initial pin weight (gm.)	Final pin weight (gm.)	Weight loss (gm.)
MO	14.62473	14.59214	0.03259
MO +0.2 wt.%. graphite	14.82935	14.82807	0.00128
MO + 0.05 wt.%. CuO	14.79014	14.7601	0.03004
MO + 0.1 wt.%. CuO	15.63315	15.61239	0.02076
MO + 0.15 wt.%. CuO	15.83103	15.81949	0.01154
MO + 0.2 wt.%. CuO	15.33835	15.33704	0.00131

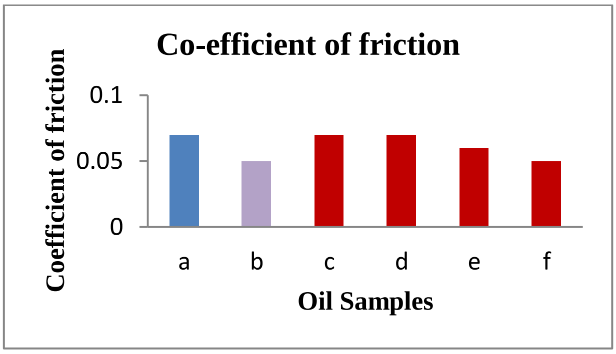


Fig. 3. Coefficient of friction of (a) pure mineral oil, (b) mineral oil+0.2 wt.% graphite, (c) mineral oil+0.05 wt.% CuO nano particles, (d) mineral oil+0.1 wt.% CuO nano particles, (e) mineral oil+0.15 wt.% CuO nano particles, (f) mineral oil+0.2 wt.% CuO nano particles.

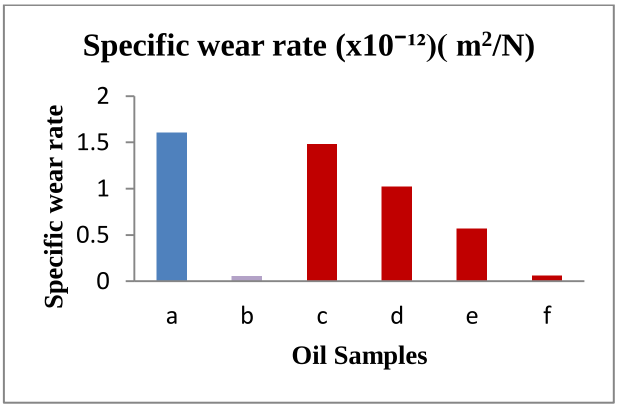


Fig. 4. Coefficient of friction of (a) pure mineral oil (b) mineral oil+0.2 wt.% graphite, (c) mineral oil+0.05 wt.% CuO nano particles, (d) mineral oil+0.1 wt.% CuO nano particles, (e) mineral oil+0.15 wt.% CuO nano particles, (f) mineral oil+0.2 wt.% CuO nano particles.

3.4 Analysis of surface roughness

The surface roughnesses of the pins were measured with a surface roughness tester (Make: Time. Model TR200) in order to evaluate the surfaces during lubrication test. Surface roughness influences the formation of a stable film thus, higher the surface roughness lesser are the chances for stable lubricant film formation.

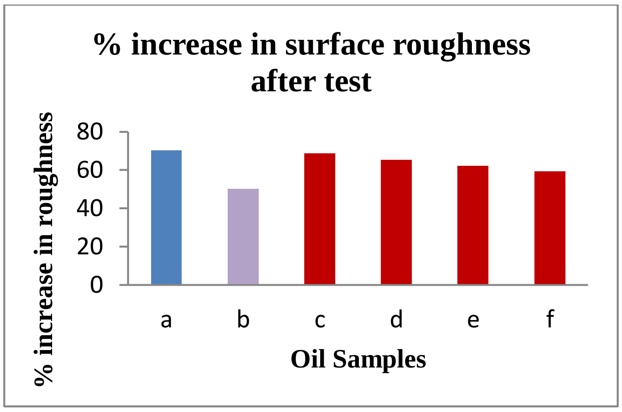
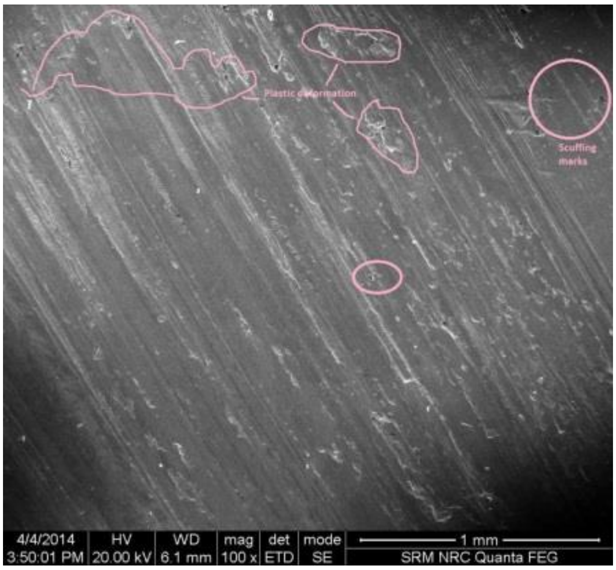
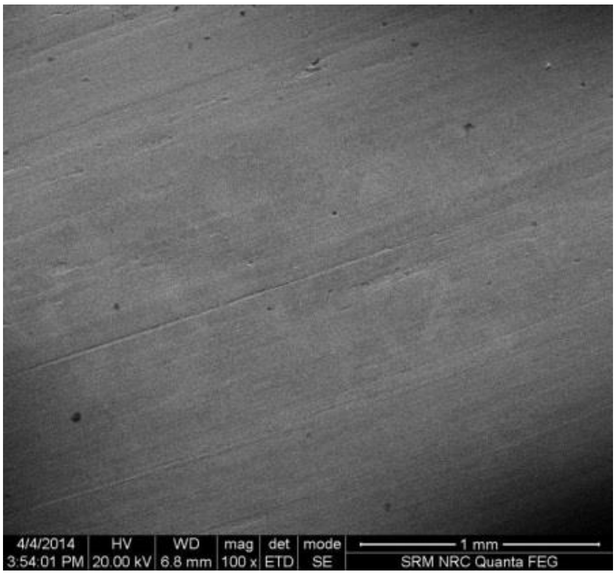


Fig. 5. Percentage increase in surface roughness (a) pure mineral oil, (b) mineral oil + 0.2 wt.% graphite, (c) mineral oil+0.05 wt.% CuO nano particles, (d) mineral oil+0.1 wt.% CuO nano particles, (e) mineral oil+0.15 wt.% CuO nano particles, (f) mineral oil+0.2 wt.% CuO nano particles.

As observed from Fig. 5, though there was an increase in surface roughnesses for all the samples but the roughnesses in case of graphite and 0.2 wt.%. CuO nano particles were much lesser as compared with that of pure mineral oil.



(a)



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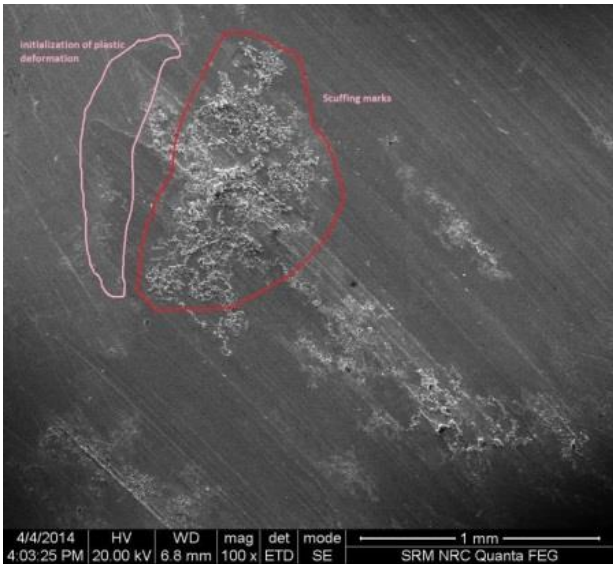

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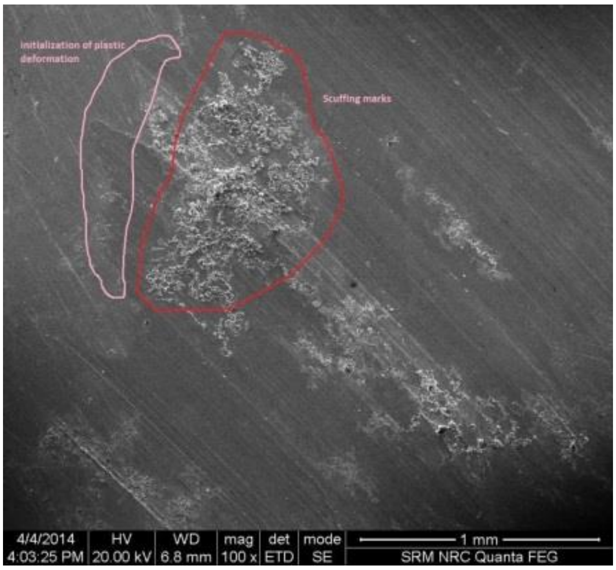

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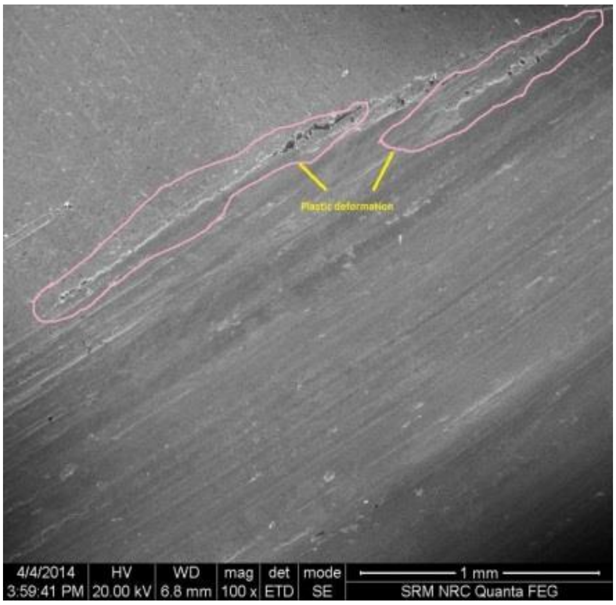

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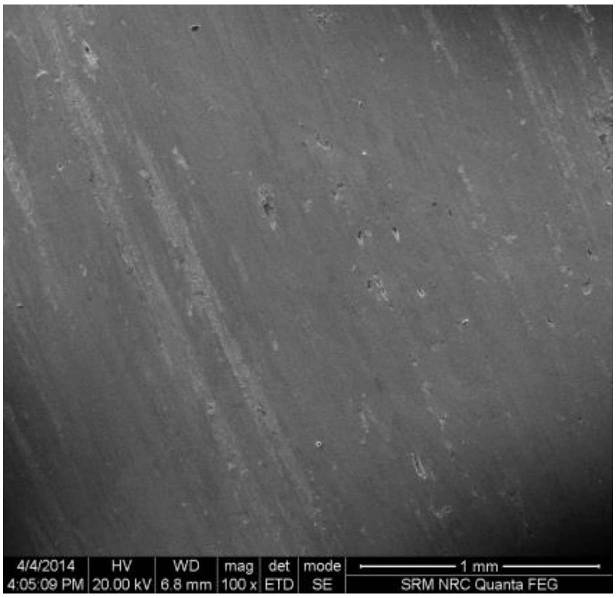
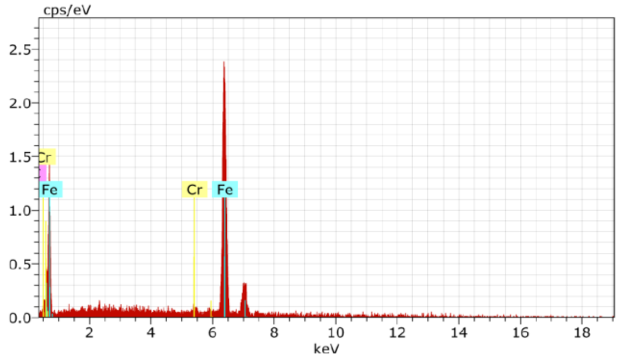


(f)

Fig. 6. SEM images (a) pure mineral oil (b) mineral oil+0.2 wt.% graphite, (c) mineral oil+0.05 wt.% CuO nano particles, (d) mineral oil+0.1 wt.% CuO nano particles, (e) mineral oil+0.15 wt.% CuO nano particles, (f) mineral oil+0.2 wt.% CuO nano particles.

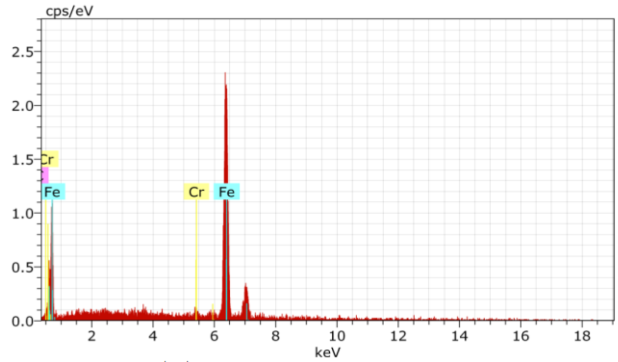
As observed from the scanning electron microscope images (Fig. 6) plastic deformations and scuffing marks were seen in case of pure mineral oil pin samples. Scuffing marks and plastic deformations were also observed in some CuO nano-particles based samples (0.05 wt.%, 0.1 wt.% and 0.15 wt.%) while graphite and 0.2 wt.% CuO nano particles based lubricants showed almost negligible scuffing marks and plastic deformations.



Spectrum: training

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Fe	26	K-series	76.80	90.14	68.31	2.38
C	6	K-series	7.44	8.73	30.77	3.54
Cr	24	K-series	0.96	1.12	0.91	0.12
		Total:	85.20	100.00	100.00	

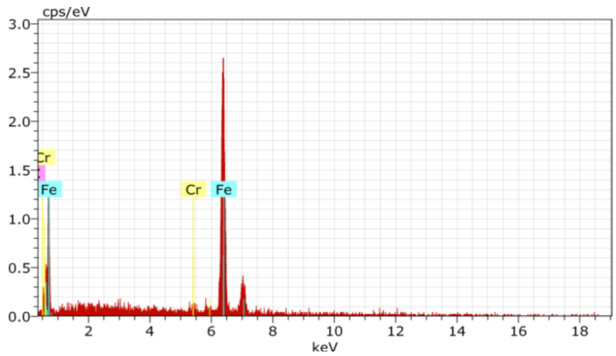
(a)



Spectrum: training

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Fe	26	K-series	67.64	81.34	49.63	2.10
C	6	K-series	14.54	17.48	49.60	5.01
Cr	24	K-series	0.98	1.18	0.77	0.12
		Total:	83.16	100.00	100.00	

(b)



Spectrum: training

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Fe	26	K-series	83.03	93.42	78.19	2.73
C	6	K-series	4.72	5.31	20.67	3.39
Cr	24	K-series	1.13	1.27	1.14	0.16
		Total:	88.88	100.00	100.00	

(c)

Fig. 7. EDS analysis of pin tested with (a) pure mineral oil, (b) mineral oil with graphite (0.2 wt.%), (c) mineral oil with CuO nanoparticles (0.2 wt.%).

From the EDS results (Fig. 7), it was observed that no CuO nanoparticles were deposited on the pin surfaces. Thus, the mechanism may be more of rolling of CuO nano particles than forming a layer or mending the surfaces as in case of graphite. But the lesser coefficient of friction, roughness and specific wear rate values as observed inferred that CuO oxide nano particles behaved as a third body between two mating parts and prevented metal-metal contact which in turn reduced wear rate. Moreover, maybe due to much lesser concentrations of CuO nano particles, they did not form a tribo layer between mating parts and had passed down in sliding by wear debris removal. Furthermore, it was observed from EDS results that carbon wt. % on the pin surface in case of mineral oil + graphite sample were more than pure mineral oil and mineral oil+ CuO nanoparticles. Thus, graphite may have formed a protective film [4-8] over the mating parts thus, reducing the coefficient of friction and specific wear rate.

4. CONCLUSION

The following can be concluded from the present work:

- The antiwear properties of mineral oils were enhanced by using CuO nano particles and graphite macro particles.
- Viscosity increased with the increase in concentration of additives. CuO nanoparticles based lubricant had higher viscosity and viscosity index as compared to graphite and pure mineral oil.
- Flash point decreased as the concentration of CuO nanoparticles increased but fire point increased. The addition of alkane group may have caused the decrease in flash point.
- The specific wear rate in case of graphite sample was lesser than CuO nanoparticles based samples and pure mineral oil.
- The COF in case of 0.2 wt.% graphite was lesser than pure mineral oil and mineral oil containing CuO nano particles (0.05 wt.%, 0.10 wt.%, 0.15 wt.%) but was comparable with 0.2 wt.% CuO nano particles based sample. There was a reduction in both coefficient of friction (28.5 % approx.) and specific wear rate (70 % approx.) in case of CuO nanolubricants and graphite based mineral oil as compared with the pure mineral oil but coefficient of friction and specific wear rate in both the cases of 0.2 wt.% CuO and 0.2 wt.% graphite were almost equal.
- Mechanisms such as rolling, mending and protective layer formation of nanoparticles between the mating surfaces could be responsible for reducing the specific wear rate and COF.
- As observed from SEM images, the pin surfaces were rougher with more scuffing marks in case of mineral oil as compared to additives based samples.
- Roughnesses of the pins increased in all cases but were less in case of graphite (0.2 wt.%) and CuO (0.2 wt.%) as compared to that of pure mineral oil.
- As observed from the present work minimum 0.2 wt.% CuO nanoparticles were required to enhance the anti-wear properties of the lubricant.

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